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Investigation of the mechanical properties of GNP/MWCNT reinforced PA66 hybrid nanocomposites

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Abstract. The multifunctional characteristics of nanocomposites have introduced novel possibilities for different industrial sectors. However, the stable and optimized production of polymeric nanocomposite components is challenging. This research investigates the mechanical behavior of thermoplastic based nanocomposites reinforced with two prominent nanofillers namely Multi Walled Carbon Nanotubes (MWCNT) and Graphene NanoPlatelets (GNP) manufactured through industrially viable methods. Three main groups of Polyamide (PA 66) based nano- and hybrid-composite specimens namely PA 66/MWCNT, PA 66/GNP, and PA 66/MWCNT/GNP are prepared. Different contents and mixture ratios of the nanofillers are incorporated in the polymeric matrix through the dilution process using a twin-screw extruder. The influence of the manufacturing parameters and content of the nanofillers on the mechanical properties of the nanocomposite specimens are investigated. Results show that the inclusion of either of the nanomaterials improves the elastic modulus and tensile strength of the nanocomposites significantly. Moreover, the combination of the two nanofillers in the nanocomposites is resulting into completely novel material properties which do not follow the linear combinations of the observed behaviors. In fact, the interaction between the two different nanofillers influences both dispersion state and mechanical properties. The mechanisms of modulation in the properties and dispersion states are also discussed using scanning electron microscopy and rheological investigations. The research provides an insight to manufacture tailored hybrid nanocomposites with the optimized mechanical properties.

Keywords: Nanocomposites, Mechanical properties, nano fillers, rheology.

INTRODUCTION

Novel nanomaterials and their corresponding composites have introduced new functionalities for different applications. Carbon nanotubes (CNTs) and Graphene nano Platelets (GnPs) due to presenting a variety of outstanding properties including very high mechanical (Elastic modulus ~1 TPa), electrical (~0.1 μΩcm), and thermal (~ 6000 W/mK) properties, etc. are being developed and utilized for many novel applications [1,2]. In order to exploit the advantages of these nanofillers in many applications, they should be effectively incorporated within a polymeric matrix. Several methods are being applied to mix the nanofillers with the polymeric matrix to produce the desired nanocomposites such as direct mixing, solution mixing, wet mixing, melt mixing, and in-situ polymerization [3]. In fact, attaining proper de-agglomeration and dispersion within the polymer matrix is crucial to reach the desired properties in the realm of nanocomposites [4]. Although, some mixing methods like solution mixing have shown promising results in the aspect of dispersion state of the nanofillers, they present some major drawbacks. Using large amounts of solvents, poor solubility of many polymers in the currently used solvents, and damaging nanofillers in addition to environmental issues make solution mixing not the preferable approach especially at the industrial scales [5]. In comparison, melt mixing provides several advantages such as creating considerably less pollutant residuals, mass production, high speed, and lower costs making it favored especially in the industrial scales. This process consists of melting the selected polymer at high temperatures and mixing it with the defined amount of nano additives through rotational and shear forces to reach the desirable content of the nanofillers within the composite. However, the quality of the products of this process depends on the parameters such as polymer characteristics, compatibility of the nanofiller and matrix, interface behavior, etc. [6]. Reaching to an acceptable state of dispersion in the composites reinforced with the CNTs and/or GnPs can be a challenging task due to their high interfacial energy. In fact, due to their very small dimensions and high aspect ratios, the attractive forces arising from Vander Waals and π-π interactions make de-agglomeration so difficult. Inclusion of the second nanofiller inside the microstructure of the nanocomposites have shown some improvement in the properties of the composites

[7–9]. It is speculated that the simultaneous presence of the two nanofillers can help homogenization of the whole microstructure through interfering in the attractive interfacial forces leading to enhanced interfaces.
The purpose of this study is to investigate of the influence of the addition of the second nanofiller on the dispersion state and the mechanical properties of the hybrid nanocomposites. Carbon nanotubes and Graphene interactions within the polymeric matrixes are investigated through their mechanical performances. Moreover, the underlying mechanisms are investigated through scanning electron microscopy and rheological analyses.

EXPERIMENTS

Materials

The selected matrix for the nano and hybrid composites is a Polyamide or Nylon (PA 6,6) from ALBIS Plastic GmbH (Tg = 54.8 oC, Tm = 262.9 ^{o}C). The MWCNTs used in this study are catalytic chemical vapor deposition produced thin MWCNTs (NC 7000 ^{TM}) by Nanocyl SA, Belgium, with the average aspect ratio of 67 (dave=10.4 nm). In addition, Graphene nanoplatelets with the average surface area of 500 m^2/g, and the size range of 100 nm to 1 μm (XGnP®) were also acquired from XGSciences, USA in an initially agglomerated state. PA 6,6 based masterbatch containing 15.0 wt. % of the aforementioned MWCNTs (according to the supplier Nanocyl SA) was also used in the manufacturing process.

Processing

A conical counter rotating twin-screw extruder (HAAKETM Rheomex CTW, Φ=31.8/20 mm rear/front, L=300 mm) was selected to perform the melt mixing process. Prior to feeding the materials to the extruder, the neat polymer, masterbatch and/or GNP nanofillers were dried, weighted, and hand-mixed in the sealed bags, respectively. Two series PA 66 based nanocomposites with the contents of 1.0, 3.0, and 6.0 wt. % of either MWCNT or GnP were produced. In addition, hybrid nanocomposites comprising different ratios MWCNTs and Graphene nanoplatelet were produced. The ratios of MWCNT to GNP within the polymeric composition of the hybrid nanocomposites were 1.0/2.0, 2.0/1.0, and 3.0/3.0 wt. %. During the blending process in the twin screw extruder, the temperature distribution was kept from 265 to 280 ^{o}C(feed section to die), with the average temperature of 275 ^{o}C.

Injection molding of the nanocomposite specimens was performed on Ferromatik, Milacron moulding machine following the instructions of ISO 294-1 standard. The geometry of the cavity of the mold was dog-bone shape which was designed based on ISO 527-2 2012 standard. At each experiment after reaching stability, 35 samples were acquired and stored in vacuum bags. Constant cooling time of 10 s was applied for all the moulding experiments.

Characterization

In order to characterize the mechanical properties of the injection-molded specimens, uniaxial tensile experiments were conducted according to ISO 527-1 2012 standard. From each series of specimens produced with the defined setting and content, 10 samples were selected randomly, and tested in the dry as molded state.

Furthermore, in order to study the dispersion state and other possible involved mechanisms in the behavior of the nanocomposites produced via different methods, scanning electron microscopy (SEM) (Quanta FEG 200 ESEM) was employed on the fractured surfaces of the nanocomposites using a charging method. Melt rheological properties of the nanocomposites were also acquired from experiments conducted using a Discovery HR-2 (TA Instruments). In order to prepare the 25 mm disc-shape samples, granulates of nanocomposites were compression molded between the preheated plates for 6 min. Subsequently, the oscillatory shear measurements were performed under nitrogen atmosphere, using 25 mm parallel plates with 1.0 mm gap in between. Each experiment was conducted on the three different samples using strains within the linear viscoelastic range, which had already been defined using strain amplitude sweeps.

RESULTS AND DISCUSSIONS

Mechanical Properties

Effect of Single Nanofiller Inclusion

In order to understand how the individual inclusion of the introduced nanofillers in the composites influences the mechanical properties of the nanocomposites, PA 66 based composites comprising different contents of either MWCNTs or XGnPs were produced and studied in the first step. Fig. 1 (a) and (b) show the Influence of the MWCNT and XGnP addition on the elastic moduli and tensile strengths of the nanocomposites, respectively. Results show that incorporation of either of the nanofillers in the polymeric matrix increases the elastic moduli consistently. In fact, addition of the 6.0 wt. % nanofillers in the nanocomposites lead to 45 and 41 % increase in the elastic moduli of the nanocomposites containing XGnPs, and MWCNTs, respectively. As it is evident from the Fig. 1 (a), the nanocomposites reinforced by Graphene Nano platelets were showing higher values in the similar contents compared to the ones reinforced with carbon nanotubes. In contrast, tensile strengths of nanocomposites reinforced with MWCNTs were higher in all the investigated nanofiller contents. It is also noteworthy to mention that in the both nanocomposite types, contents higher than 3.0 wt. % nanofiller inclusion resulted into lower tensile strengths indicating larger agglomeration sites and/or less control on the alignment along the flow.

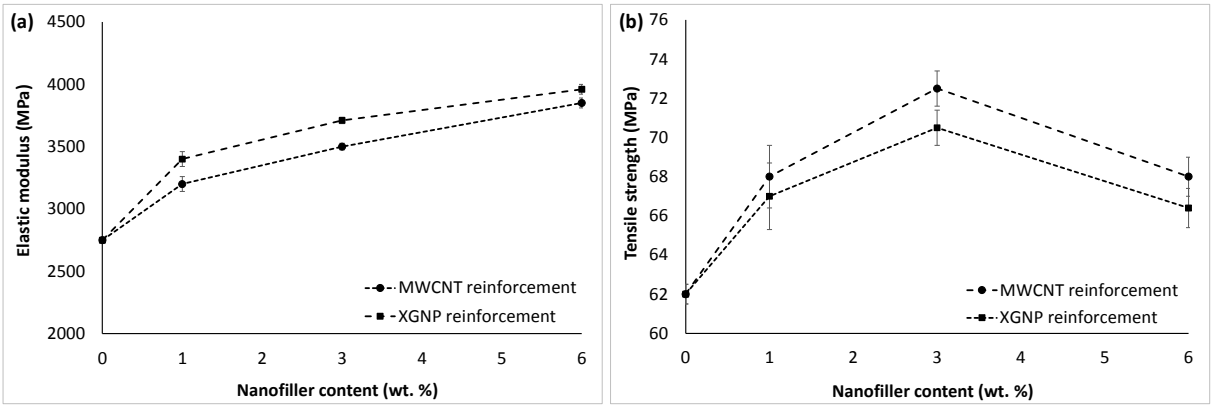

FIGURE 1. Influence of the MWCNT and XGnP content on the (a) Elastic moduli, and (b) tensile strengths of the corresponding nanocomposites.

Interaction between the Two Nanofillers

In the second step, PA 66 based nanocomposites containing both MWCNTs and XGnPs were produced and investigated. The reason behind this study was to investigate whether simultaneous presence of the nanofillers can result into improved dispersion and mechanical properties or not. Fig. 2 shows the comparison between the 3.0 wt. % nanofiller reinforced nanocomposites containing either or both of the nanofillers. Results show that replacing 1.0 wt. % carbon nanotubes with Graphene Nano platelets lead to notable increase in both elastic modulus and tensile strength compared to nanocomposites containing 3.0 wt. % of MWCNTs or XGnPs. However, replacing 1.0 wt. % Graphene Nano platelets with carbon nanotubes decreased the tensile strength values. It seems when the nanocomposite system is dominated by the carbon nanotubes, the system can benefit from the addition of the second nanofiller effectively.

In order to understand the interaction between the two nanofillers within the polymeric matrix better, nanocomposites containing 6.0 wt. % of the nanofillers were also studied (see Fig. 2(c) and (d)). Similar to the nanocomposites containing 3.0 wt. % nanofillers, the elastic modulus increased with introducing the second nanofiller in the nanocomposite system. However, the resulted tensile strength was less than when both nanocomposites were filled with just one type the nanofillers.

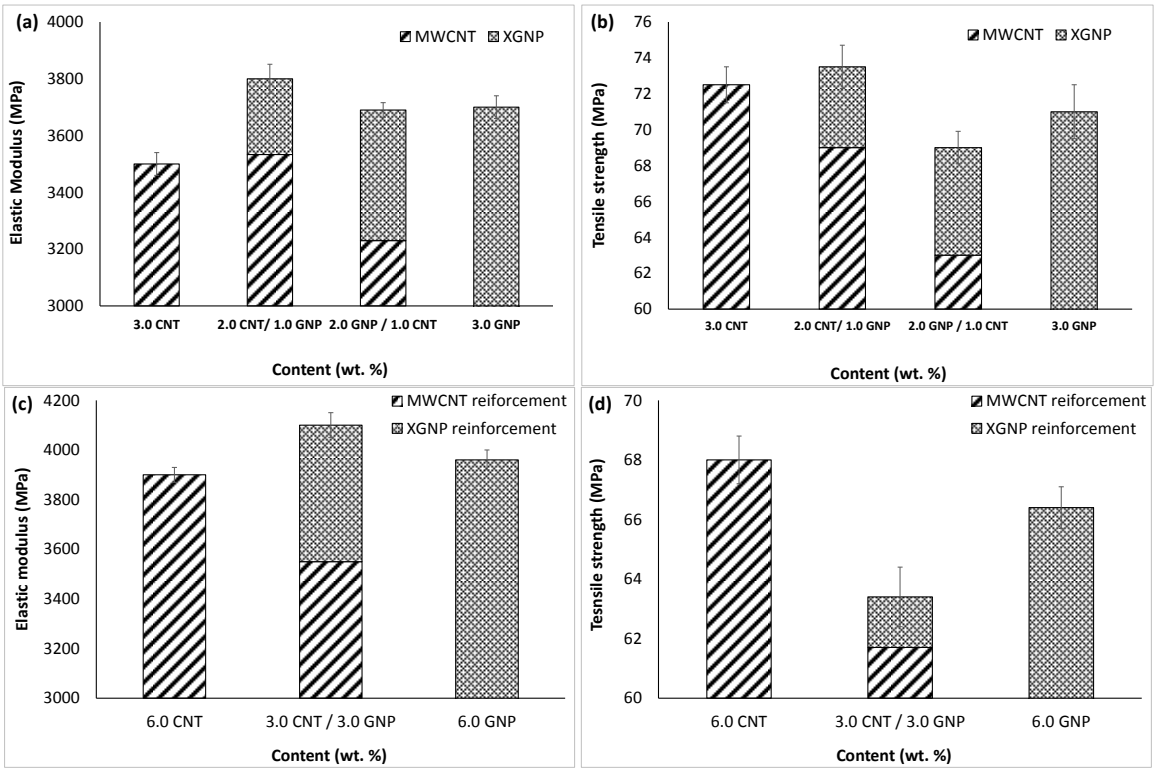

FIGURE 2. Mechanical properties of the respectively 3.0 and 6.0 wt. % nanofiller reinforced nanocomposites as the function of MWCNT / XGnP inclusion within the PA 66 matrix: (a), (c) elastic moduli, (b), (d) tensile strengths.

Rheological Investigations

Fig. 3 shows the influence of the type and content of the nanofillers within the polymeric matrix on the complex viscosity of the nanocomposites. The rheological behavior of the presented 3.0 and 6.0 wt. % nanofiller reinforced nanocomposites were investigated. As it can be seen from the figures, nanocomposites containing carbon nanotubes showed significantly higher viscosities compared to the nanocomposites containing Graphene Nano platelets. In the all nanocomposites, the Newtonian plateau was not present, and only the shear thinning is defining the melt behavior, while the viscosity decreases constantly with the increase of frequency.

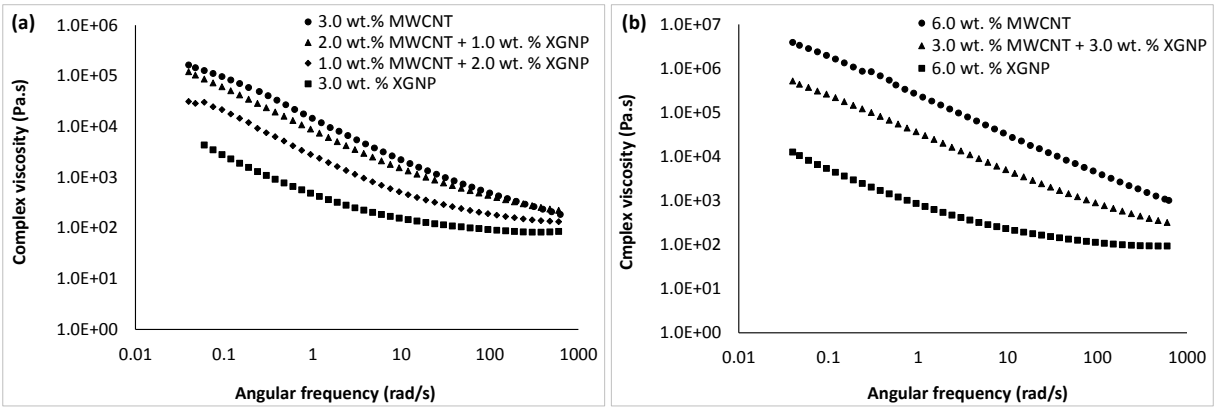

FIGURE 3. Complex viscosity of the (a) 3.0 and (b) 6.0 wt. % nanofiller reinforced nanocomposites as a function of MWCNT/ XGnP inclusion ratio and angular velocity.

Microstructure

Fig. 4 shows the SEM pictures of the nanocomposite microstructures. As it can be noticed from the pictures, in the both nanocomposites, acceptable states of dispersion have been achieved, indicating the successful mixing and injection molding process. An interesting observation was made in the Fig. 4(b), where the graphene nanoplatelets have been placed between the carbo nanotubes prohibiting the nanofillers to agglomerate additionally. Regarding the attained states of dispersion, one might assume that the nucleation influence of the carbon nanotubes in the composites might be reason for higher values of the tensile strengths.

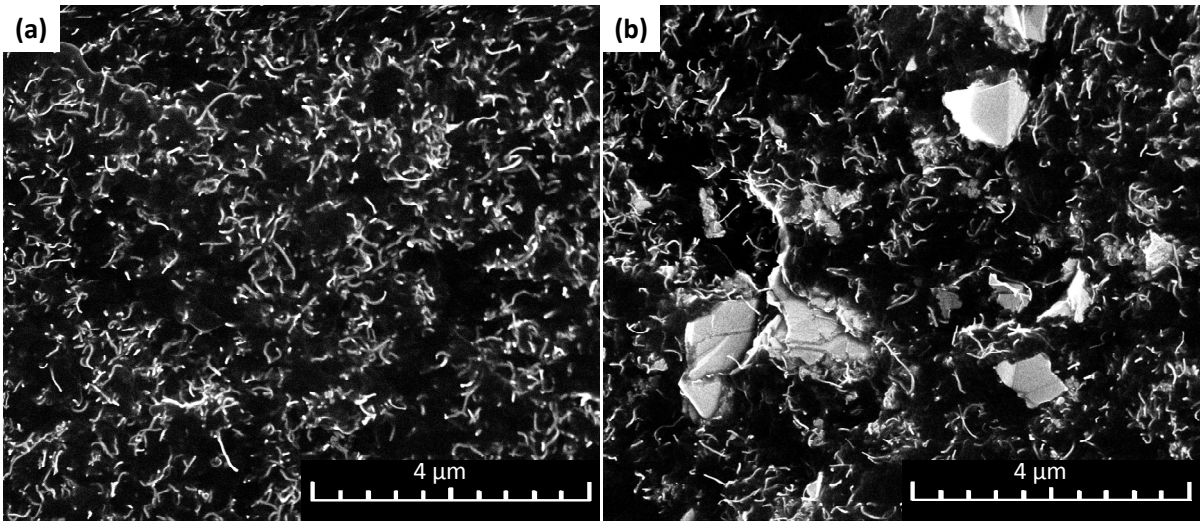

FIGURE 4. Scanning electron microscopy investigation of the (a) carbon nanotubes and (b) hybrid MWCNT/XGnP nanocomposites.

CONCLUSIONS

PA 66 based hybrid and nano composites containing different contents of carbon nanotubes and Graphene nano platelets were produced via melt blending and injection molding. Results showed that addition of the nanofillers increased the tensile strength and elastic moduli of the nanocomposites. Moreover, inclusion of the smaller percentage of the XGnPs in the MWCNTs reinforced composites additionally improved the mechanical properties. In fact, the novel hybrid composites showed enhanced mechanical properties compared to the nanocomposites with the similar content of just one type of nanofillers. The reasons behind the improvement were also investigated through rheological and electron microscopy tools.

REFERENCES

1. J. Hone, M. Whitney, C. Piskoti, A. Zettl, *Phys. Rev. B.* **59**, R2514 (1999).
2. M. Meyyappan, Carbon Nanotubes: Science and Applications, CRC Press, 2004.
3. P. M. Ajayan, L. S. Schadler, P. V Braun, Nanocomposite Science and Technology, Wiley, 2003.
4. E. Alishahi, S. Shadlou, S. Doagou-R, M. R. Ayatollahi, *Macromol. Mater. Eng.* **298** (2013).
5. E. Thostenson, C. Li, T. Chou, *Compos. Sci. Technol.* **65**, 491–516 (2005).
6. S. Doagou-Rad, A. Islam, J. S. Jensen, *Procedia CIRP.* **66**, 131–136 (2017).
7. J. Sumfleth, X. C. Adroher, K. Schulte, *J. Mater. Sci.* **44**, 3241 (2009).
8. M. H. Al-Saleh, *Synth. Met.* **209**, 41–46 (2015).
9. Ren P, Di Y, Zhang Q, Li L, Pang H, Li Z, *Macromol. Mater. Eng.* **297**, 437–443 (2012).